The changing nature of the Pb-206/Pb-207 isotopic ratio of lead in rainwater, atmospheric particulates, pine needles and leaded petrol in Scotland, 1982-1998

The changing nature of the $^{206}Pb/^{207}Pb$ isotopic ratio of lead in rainwater, atmospheric particulates, pine needles and leaded petrol in Scotland, 1982–1998

John G. Farmer,*[a] Lorna J. Eades,[a] Margaret C. Graham[a] and Jeffrey R. Bacon[b]

[a]*Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ*
[b]*Soil Science Group, Macaulay Land Use Research Institute, Craigiebuckler, Aberdeen, UK AB15 8QH*

Received 17th September 1999, Accepted 14th December 1999

The inductively coupled plasma-mass spectrometry (ICP-MS)-determined $^{206}Pb/^{207}Pb$ ratio of 145 samples of rainwater collected at 25 locations around Scotland during December 1997 and January 1998 and at three long-term monitoring stations in the northeast, central belt and southeast of the country from November 1997 to December 1998 averaged 1.144 ± 0.017 (1 *s*). This represents a significant increase from the mean value of 1.120 ± 0.016 recorded for the long-term sites in 1989–1991, only partly attributable to a concomitant increase in the $^{206}Pb/^{207}Pb$ ratio of leaded petrol from 1.075 ± 0.013 to 1.088 ± 0.007. The rainwater $^{206}Pb/^{207}Pb$ data for the late 1990s also contrast markedly with the lower $^{206}Pb/^{207}Pb$ ratios found for pine needle and atmospheric particulate samples from Scotland (*e.g.* Glasgow: 1.085 ± 0.012 in 1985–1986, 1.099 ± 0.007 in 1991–1992), England and Western Europe in this study for the period 1982–1992 when emissions of lead to the atmosphere from petrol-engined vehicles in the UK were ~2–9 times higher. The observed change in the lead isotopic signature of rainwater predominantly reflects the impact of measures, such as the introduction and growing uptake of unleaded petrol, to reduce car exhaust emissions of lead to the atmosphere in the UK. Based on the rainwater data, source apportionment calculations suggest a general decline in the contribution of leaded petrol to atmospheric lead in Scotland from 53–61% in 1989–1991 to 32–45% in 1997–1998, with a corresponding decline in the urban environment from 84–86% to 48–58%.

Introduction

The aim of this study was to determine the stable lead isotopic signature ($^{206}Pb/^{207}Pb$) of rainwater in Scotland in the late 1990s and to compare the findings with corresponding data for rainwater and atmospheric particulates collected since the 1980s and for different sources of environmental lead, with a view to evaluating the impact of measures to reduce emissions of lead to the atmosphere, such as the introduction and increasing use of unleaded petrol.

There are four stable isotopes of primordial lead, namely ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. The last three isotopes, however, are also radiogenic, formed by radioactive decay in the ^{238}U (half-life 4.5×10^9 years), ^{235}U (half-life 0.7×10^9 years) and ^{232}Th (half-life 14.1×10^9 years) decay series, respectively. The abundance of lead isotopes in minerals and ores is determined by the original uranium to thorium ratio, time of formation and lead concentration of the material. While the average present-day crustal abundances of these isotopes yield a mean $^{206}Pb/^{207}Pb$ ratio of 1.20 ± 0.015, there is a much wider range found for lead ore deposits around the world, *e.g.* 1.04 for Broken Hill, Australia, 1.17 for Leadhills, Scotland, and 1.39 for Mississippi Valley, MO, USA.[1,2]

The lead ore deposits from Australia have been used, along with Canadian lead ($^{206}Pb/^{207}Pb = 1.16$), by Associated Octel to produce alkyllead anti-knock additives ($^{206}Pb/^{207}Pb \sim 1.07$) for petrol consumed in the UK.[3] The significant difference between the $^{206}Pb/^{207}Pb$ ratio of the lead emitted by car exhausts and those of other sources of anthropogenic lead, *e.g.* coal burning ($^{206}Pb/^{207}Pb \sim 1.18$), has afforded an opportunity, at least in principle, for the quantitative assessment of the relative contributions from specific sources to the environmental lead burden.[4–6] Thus, $^{206}Pb/^{207}Pb$ ratio variations have been recorded and used in numerous parts of the world, where different characteristic isotopic signatures may prevail, in such studies on a wide range of materials, including atmospheric aerosols,[4,7–14] lake sediments,[15–17] peat bogs,[17–20] soils,[21–23] grass,[24] tree rings,[25,26] moss[27,28] and ice cores.[29,30] They have also been used to trace air mass movement[31–33] and oceanic transport phenomena[34] as well as the environmental fate and behaviour of anthropogenic lead.[35–38]

In the UK, measures introduced in 1986 to reduce the maximum permitted concentration of lead in petrol from 0.40 to $0.15\ g\ l^{-1}$ and to promote the use of unleaded petrol have resulted in a reduction of emissions of lead from petrol-engined vehicles to the atmosphere from an estimated 6.5×10^3 tonnes in 1985 to 0.8×10^3 tonnes in 1997.[39] Resultant changes in source apportionment of atmospheric lead with time and the use of the $^{206}Pb/^{207}Pb$ ratio as a tracer are dependent upon the monitoring of stable lead isotopic ratios in the atmosphere and in contributory sources such as leaded petrol. This paper presents isotopic data for rainwater in Scotland in 1997–1998, directly determined by the technique of inductively coupled plasma-mass spectrometry (ICP-MS),[40] and interprets them in the context of additional long-term data for leaded petrol from 1989–1998 and for rainwater, atmospheric particulates and pine needles collected at various locations in Scotland and elsewhere during the period 1982–1992.

Experimental

Sample collection and preparation

Petrol samples (100 ml) ($n = 33$) were collected directly at brand-name pumps in Edinburgh on dates between February 1989 and November 1998 as shown in Table 1 and the lead was

Table 1 $^{206}Pb/^{207}Pb$ ratios in leaded petrol collected in Edinburgh,[a] 1989–1998

Brand of petrol	Date of collection	$^{206}Pb/^{207}Pb$ (± 1 *s*)
	Feb. 1989	1.056 ± 0.001
	Dec. 1989	1.066 ± 0.007
Mean	(1989)	*1.061 ± 0.0071*
BP	Dec. 1990	1.069 ± 0.002
Jet	Dec. 1990	1.074 ± 0.003
Shell	Dec. 1990	1.062 ± 0.004
Texaco	Dec. 1990	1.083 ± 0.001
Mean	(1990)	*1.072 ± 0.0088*
Savacentre	May 1991	1.093 ± 0.003
Savacentre	Dec. 1991	1.088 ± 0.002
Texaco	Dec. 1991	1.084 ± 0.002
Mean	(1991)	*1.088 ± 0.0045*
Savacentre	Nov. 1993	1.070 ± 0.003
Gulf	Dec. 1993	1.067 ± 0.003
Gulf	Jan. 1994	1.067 ± 0.005
Savacentre	Jan. 1994	1.067 ± 0.004
Texaco	Jan. 1994	1.075 ± 0.002
Mean	(1993–1994)	*1.069 ± 0.0035*
BP	Oct. 1994[a]	1.063 ± 0.003
Gulf	Nov. 1994	1.062 ± 0.002
Jet	Nov. 1994	1.068 ± 0.003
Texaco	Nov. 1994	1.065 ± 0.003
Mean	(1994)	*1.065 ± 0.0026*
BP	Feb. 1996	1.076 ± 0.001
Jet	Feb. 1996	1.092 ± 0.003
Shell	Feb. 1996	1.080 ± 0.002
Mean	(1996)	*1.083 ± 0.0083*
BP	Mar. 1997	1.074 ± 0.005
Esso	Mar. 1997	1.076 ± 0.004
Savacentre	Mar. 1997	1.073 ± 0.001
Shell	Mar. 1997	1.072 ± 0.005
Mean	(Early 1997)	*1.074 ± 0.0017*
Safeway	Nov. 1997	1.083 ± 0.0017
Savacentre	Nov. 1997	1.097 ± 0.0011
Shell	Nov. 1997	1.098 ± 0.0014
Texaco	Nov. 1997	1.075 ± 0.0013
Mean	(Late 1997)	*1.088 ± 0.0111*
BP	Nov. 1998	1.085 ± 0.0012
Jet	Nov. 1998	1.086 ± 0.0014
Savacentre	Nov. 1998	1.088 ± 0.0011
Shell	Nov. 1998	1.089 ± 0.0008
Mean	(1998)	*1.087 ± 0.0018*
Mean	($n = 33$)	*1.076 ± 0.011*

[a]The Oct. 1994 petrol sample was collected in Ullapool, northwest Scotland.

Table 2 $^{206}Pb/^{207}Pb$ ratios in rainwater from Scotland, December 1997–January 1998

Location	December 1997 $^{206}Pb/^{207}Pb$ (± 1 *s*)	January 1998 $^{206}Pb/^{207}Pb$ (± 1 *s*)
1. Reay	1.160 ± 0.0098	1.154 ± 0.0058
2. Fort Augustus	1.147 ± 0.0095	1.133 ± 0.0074
3. Tarland	1.160 ± 0.0035	1.144 ± 0.0079
4. Tobermory	1.150 ± 0.0090	1.154 ± 0.0074
5. Kilmalieu	1.152 ± 0.0094	1.156 ± 0.0039
6. Oban	1.144 ± 0.0049	1.149 ± 0.0027
7. Bridge of Earn		1.123 ± 0.0023
8. Dundee	1.161 ± 0.0012	1.150 ± 0.0092
9. St. Andrews	1.151 ± 0.0019	1.144 ± 0.0042
10. Ceres		1.147 ± 0.0084
11. Kinross	1.128 ± 0.0010	1.131 ± 0.0008
12. Menstrie	1.131 ± 0.0037	1.133 ± 0.0055
13. Stirling	1.147 ± 0.0042	1.218 ± 0.0072
14. Buchlyvie	1.137 ± 0.0032	1.112 ± 0.0028
15. Paisley		1.147 ± 0.0027
16. Giffnock	1.139 ± 0.0024	1.133 ± 0.0037
17. East Kilbride	1.141 ± 0.0071	1.117 ± 0.0057
18. Livingston	1.121 ± 0.0037	1.127 ± 0.0081
19. Edinburgh A	1.179 ± 0.0031	1.186 ± 0.0053
20. Edinburgh B	1.155 ± 0.0004	1.207 ± 0.0005
21. Kilmarnock A	1.143 ± 0.0026	1.125 ± 0.0032
22. Kilmarnock B	1.139 ± 0.0049	1.132 ± 0.0045
23. Ayr	1.152 ± 0.0023	1.136 ± 0.0059
24. Loch Bradan	1.122 ± 0.0017	1.119 ± 0.0012
25. Dumfries	1.131 ± 0.0030	1.123 ± 0.0057
Mean	*1.145 ± 0.014*	*1.144 ± 0.026*

extracted using the iodine monochloride/solvent extraction method of Price,[41] prior to final solution preparation in 2% v/v (0.32 M) nitric acid for analysis.

Rainwater samples were collected by one of three methods. For the samples ($n = 47$, Table 2) collected during December 1997 and January 1998 from 25 sites around Scotland (Fig. 1), 1 l polypropylene bottles (Merck, Poole, Dorset, UK), each with a 14 cm diameter polypropylene filter funnel taped to its rim, were placed at least 3 m above the ground, usually in a domestic garden away from obstruction and possible contamination. For the samples ($n = 98$, Table 3) collected on a regular basis between November 1997 and December 1998 at the three long-term monitoring sites specifically located away from roads and industrial activity at Glensaugh (weekly), Hartwood (monthly) and Sourhope (weekly) (Fig. 1), two methods were used.[35] The open gauge method ($n = 68$) collects rainfall (or anything that drops vertically) using shielded rain gauges designed to remove any effect of turbulence around the gauge and installed in triplicate 3 m above ground level. The filter gauge method ($n = 30$), which collects not only rainfall but also air particulates and mist that could come in sideways, uses specially adapted gauges installed in triplicate 3 m above ground level and alongside the open gauges. In theory, the open gauge samples should therefore yield the isotopic character of lead being deposited in rainwater, both dissolved and washed out particulates, whereas the filter gauge samples might indicate if there are other components preferentially intercepted by vegetation. The open filter funnel method should be intermediate between these approaches to rainfall collection.

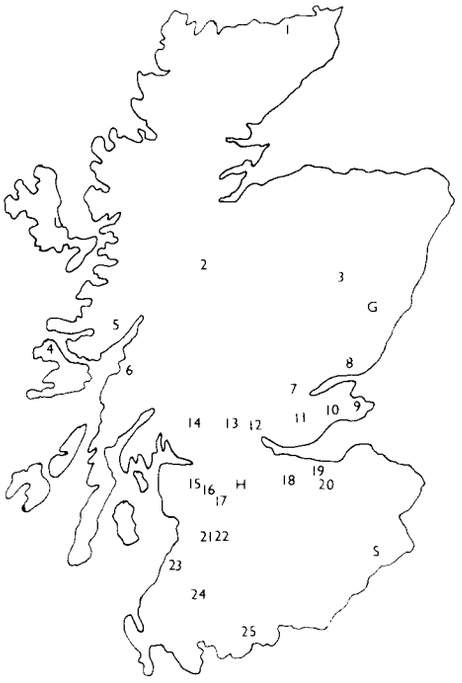

Fig. 1 Map of Scotland showing the 25 rainwater sampling locations during December 1997 and January 1998 (see Table 2 for key) and the three long-term rainwater collection sites at Glensaugh (G), Hartwood (H) and Sourhope (S).

Table 3 $^{206}Pb/^{207}Pb$ ratios in rainwater from three long-term sites in Scotland, November 1997–December 1998

	Glensaugh		Hartwood		Sourhope	
	Open gauge	Filter gauge	Open gauge	Filter gauge	Open gauge	Filter gauge
Date of collection	$^{206}Pb/^{207}Pb$ (± 1 *s*)	$^{206}Pb/^{207}Pb$ (± 1 *s*)	$^{206}Pb/^{207}Pb$ (± 1 *s*)	$^{206}Pb/^{207}Pb$ (± 1 *s*)	$^{206}Pb/^{207}Pb$ (± 1 *s*)	$^{206}Pb/^{207}Pb$ (± 1 *s*)
19 Nov. 1997	1.140±0.0039	1.144±0.0040				
26 Nov. 1997			1.168±0.0051	1.144±0.0019	1.138±0.0036	1.145±0.0039
3 Dec. 1997	1.154±0.0061	1.140±0.0021				
17 Dec. 1997	1.163±0.0047	1.155±0.0028	1.171±0.0041	1.149±0.0035	1.145±0.0032	1.153±0.0133
14 Jan. 1998	1.155±0.0051	1.158±0.0016				
21 Jan. 1998			1.180±0.0060	1.148±0.0043	1.148±0.0070	1.155±0.0069
28 Jan. 1998		1.137±0.0054				
11 Feb. 1998		1.161±0.0029				
18 Feb. 1998			1.181±0.0118	1.118±0.0109	1.152±0.0083	1.152±0.0074
25 Feb. 1998		1.140±0.0053				
11 Mar. 1998		1.138±0.0076				
18 Mar. 1998			1.207±0.0087	1.134±0.0056		1.129±0.0035
25 Mar. 1998		1.135±0.0054				
1 Apr. 1998	1.144±0.0015				1.141±0.0041	
8 Apr. 1998	1.132±0.0010	1.139±0.0033			1.135±0.0029	
15 Apr. 1998					1.141±0.0043	
22 Apr. 1998	1.139±0.0017	1.139±0.0014	1.190±0.0050	1.144±0.0018	1.142±0.0042	1.146±0.0051
29 Apr. 1998	1.140±0.0018				1.131±0.0013	
6 May 1998		1.140±0.0039				
13 May 1998			1.178±0.0015	1.143±0.0022	1.144±0.0072	1.150±0.0030
20 May 1998		1.146±0.0098				
27 May 1998	1.140±0.0022				1.134±0.0045	
3 June 1998	1.144±0.0039	1.140±0.0029			1.142±0.0051	
10 June 1998	1.140±0.0021		1.149±0.0025	1.144±0.0020	1.137±0.0035	1.142±0.0030
17 June 1998	1.138±0.0029				1.141±0.0019	
24 June 1998	1.140±0.0034					
1 July 1998	1.126±0.0019				1.136±0.0030	
8 July 1998			1.152±0.0025			
15 July 1998	1.141±0.0030				1.138±0.0046	
22 July 1998	1.136±0.0033					
29 July 1998					1.127±0.0041	
5 Aug. 1998	1.133±0.0020				1.112±0.0035	
12 Aug. 1998					1.141±0.0074	
19 Aug. 1998	1.145±0.0027		1.123±0.0024			
2 Sept. 1998					1.135±0.0016	
16 Sept. 1998					1.144±0.0020	
30 Sept. 1998					1.145±0.0017	
7 Oct. 1998	1.156±0.0014				1.151±0.0013	
14 Oct. 1998					1.153±0.0016	
21 Oct. 1998	1.113±0.0016				1.141±0.0012	
28 Oct. 1998	1.138±0.0006		1.140±0.0029			
4 Nov. 1998					1.135±0.0024	
11 Nov. 1998	1.136±0.0006				1.142±0.0033	
18 Nov. 1998	1.136±0.0011				1.137±0.0014	
25 Nov. 1998	1.142±0.0018		1.137±0.0020			
2 Dec. 1998	1.133±0.0011					
9 Dec. 1998	1.138±0.0014					
16 Dec. 1998	1.141±0.0014					
23 Dec. 1998			1.156±0.0008			
Mean	*1.140±0.010*	*1.144±0.008*	*1.164±0.024*	*1.141±0.010*	*1.140±0.008*	*1.147±0.008*

After filtering (Whatman 542, 2.7 μm, 18.5 cm diameter Maidstone, UK), sample aliquots were usually concentrated to 10% of their original volume by evaporation on a hotplate at 90 °C and acidified to 2% v/v nitric acid prior to analysis. It should be noted that most of the rainwater samples (*i.e.* from Glensaugh, Hartwood and Sourhope) were initially collected not merely for lead but for anions and basic water analysis. Thus they were not treated immediately after collection in any way other than by filtration. Although it is therefore possible that the lead concentrations of these samples may have been affected, *e.g.* by adsorption to sample container walls, the lead isotopic ratios, the focus of the work presented here, would not have been affected.

Oven-dried, powdered pine needle samples ($n=14$) for 1982–1986 from the locations in Scotland, England, Netherlands and Germany listed in Table 4 were provided by Dr. J. N. Cape, Natural Environment Research Council Institute of Terrestrial Ecology (NERC ITE), Penicuik. These samples were ashed at 450 °C, digested in 8 M nitric acid and the resultant extracts diluted in 2% v/v nitric acid for analysis.

Atmospheric particulates from ~9 m above street level in the centre of Edinburgh ($n=14$) were collected over 8 h sampling periods in 1990–1991 (Table 4) using a membrane filter of pore size 0.45 μm (Millipore, HAWP 037 00) attached to an electric pump (Millipore, XX60 220 50).[42] Other atmospheric particulate samples, similarly collected (over 1–2 week periods) in 1985–1986 from the west end of Glasgow ($n=4$) and in 1985 from rural locations (except for Devilla, Fife) in northern Scotland ($n=10$) and England ($n=5$) (Table 4), were also supplied by Dr. Cape. In addition, Mr. D. Smith, National Radiological Protection Board (NRPB), Glasgow, provided large (22 × 25 cm) high-volume air filters collected over 2 week periods in southwest Glasgow ($n=7$) in 1991–1992 and in Guernsey ($n=4$) in 1989, from which

Table 4 $^{206}Pb/^{207}Pb$ ratios in pine needles* and atmospheric particulates, 1982–1992

Location and type of sample	Date of collection	$^{206}Pb/^{207}Pb$ ($\pm 1\ s$)
*Netherlands**		
Kootwijk	1982 (growth)	1.123 ± 0.002
	1983 (growth)	1.122 ± 0.002
	1985 (growth)	1.127 ± 0.008
Rip	1984 (growth)	1.129 ± 0.003
*Germany**		
Kalbelescheuer, Black Forest	1985 (growth)	1.121 ± 0.006
	1985 (growth)	1.136 ± 0.007
N. Langebramke, Hartz Mountains	1986 (growth)	1.120 ± 0.003
Selb, E. Bavaria	1986 (growth)	1.132 ± 0.012
Mean	(1982–1986)	*1.126 ± 0.006*
*Scotland**		
Glenbranter, N.W.	1985 (growth)	1.106 ± 0.004
	1985 (growth)	1.117 ± 0.008
Darnaway, N.E.	1985 (growth)	1.111 ± 0.005
	1985 (growth)	1.117 ± 0.009
*England**		
Ashford, S.E.	1985 (growth)	1.117 ± 0.007
	1985 (growth)	1.115 ± 0.009
Mean	(1985)	*1.114 ± 0.004*
Scotland (urban)		
Glasgow	Jan. 1985	1.069 ± 0.004
	Apr. 1985	1.089 ± 0.003
	Jun. 1985	1.083 ± 0.003
	Jun. 1986	1.097 ± 0.003
Mean	(1985–1986)	*1.085 ± 0.012*
Scotland (rural)		
Banchory, Grampian	Feb./Mar. 1985	1.107 ± 0.007
	Mar. 1985	1.113 ± 0.003
Crathes, Grampian	Feb./Mar. 1985	1.128 ± 0.009
	Apr. 1985	1.121 ± 0.006
Brathens, Grampian	May 1985	1.116 ± 0.002
	June 1985	1.111 ± 0.002
	June/July 1985	1.120 ± 0.004
	July/Aug. 1985	1.122 ± 0.009
	Aug./Sept. 1985	1.119 ± 0.002
Devilla, Fife	May 1985	1.124 ± 0.004
Mean	(1985)	*1.118 ± 0.006*
England		
Gisburn, Lancashire	Mar. 1985	1.111 ± 0.004
	Apr./May 1985	1.100 ± 0.003
	Sept. 1985	1.088 ± 0.003
	Oct. 1985	1.102 ± 0.002
	Nov. 1985	1.092 ± 0.003
Mean	(1985)	*1.108 ± 0.018*
Channel Islands		
Fort Doyle, Guernsey	Jan. 1989	1.093 ± 0.003
	Feb. 1989	1.103 ± 0.004
	Mar. 1989	1.092 ± 0.006
	Apr. 1989	1.098 ± 0.006
Mean	(1989)	*1.097 ± 0.005*
Scotland (urban)		
Edinburgh	Feb. 1990	1.096 ± 0.007
	May 1990	1.069 ± 0.004
	May 1990	1.086 ± 0.005
	May 1990	1.119 ± 0.001
	May 1990	1.088 ± 0.005
	May 1990	1.086 ± 0.002
	May 1990	1.087 ± 0.002
	June 1990	1.090 ± 0.002
	June 1990	1.097 ± 0.002
	July 1990	1.094 ± 0.002
	Aug. 1990	1.090 ± 0.003
	Apr. 1991	1.092 ± 0.003
	July 1991	1.099 ± 0.019
	Nov. 1991	1.101 ± 0.006
Mean	(1990–1991)	*1.092 ± 0.011*
Scotland (urban)		
Glasgow	Jan. 1991	1.095 ± 0.003
	Apr. 1991	1.102 ± 0.004
	July 1991	1.097 ± 0.006
	Oct. 1991	1.093 ± 0.003
	Jan. 1992	1.114 ± 0.005
	July 1992	1.096 ± 0.003
	Oct. 1992	1.093 ± 0.001
Mean	(1991–1992)	*1.099 ± 0.007*

subsamples were cut. All atmospheric filters were leached with 1.6 M nitric acid and the resultant extracts diluted in 2% v/v nitric acid for analysis.

All reagents used in sample preparation were of the highest analytical quality available, *i.e.* Aristar nitric acid (Merck), and water was deionized and purified by reverse osmosis and ion exchange to 18.3 MΩ quality using a Milli-QSP system (Millipore, Watford, UK).

Sample analysis

All rainwater samples were analysed by ICP-MS using a PlasmaQuad (PQ) 3 instrument (VG Elemental, Winsford, UK), employing an rf forward power of 1350 W, reflected power of 1–3 W, argon gas flows (l min^{-1}) of 13.1, 0.76–0.79 and 0.81–0.85 for coolant, auxiliary and nebulizer, respectively, and nickel sampler and skimmer cones, with a Meinhard nebulizer, Gilson autosampler and a Gilson Minipuls 3 peristaltic pump (Anachem, Luton, UK) providing a solution uptake rate of 0.55 ml min^{-1}. The instrument was operated in peak jumping mode over the mass range 203.6–209.4 u, with one central measurement point per peak, 2 ms dwell time, 1 min acquisition time, five replicate runs per sample and pulse counting mode for ion collection. A solution of the National Institute of Standards and Technology (NIST) common lead isotopic reference standard SRM 981 ($^{206}Pb/^{207}Pb = 1.0933$) was used for calibration and mass bias correction.[42] Over a 1 year period, an average measured value of 1.094 ± 0.002 was obtained.

Petrol samples for the periods 1989 to 1991 and 1993 to early 1997 were analysed using VG PQ 1 and 2 instruments, respectively, at the Scottish Universities Research and Reactor Centre (SURRC), East Kilbride, while those for late 1997 to 1998 were analysed by the PQ 3 described above. All pine needle and atmospheric particulate samples, with the exception of those from Edinburgh (1990–1991), were analysed using the VG PQ 2 instrument.

After appropriate blank corrections corresponding to the different modes of preparation, mean internal analytical precisions [1 standard deviation (*s*)] on the measured $^{206}Pb/^{207}Pb$ ratios were $\pm 0.24\%$, $\pm 0.34\%$ and $\pm 0.42\%$ for the petrol ($n = 33$), rainwater ($n = 145$) and pine needle/atmospheric particulate ($n = 58$) samples, respectively. Mean external analytical precision on $^{206}Pb/^{207}Pb$, as determined by repeated analysis ($n = 55$) of the International Atomic Energy Agency SL-1 Lake Sediment reference material over several years, was $\pm 0.36\%$.

The results presented here are for the $^{206}Pb/^{207}Pb$ ratio, that most commonly used in environmental studies and the most relevant for the purposes of this research. Partly because of the fragmented nature of this work over several years, a complete set of data for the other lead isotopic ratios is not available.

Results

Petrol

The individual $^{206}Pb/^{207}Pb$ results ($n = 33$) for petrol collected in the Edinburgh area from February 1989 to November 1998 are listed in Table 1. The ratios ranged from 1.056 ± 0.001 (February 1989) to 1.098 ± 0.0014 (November 1997) with an overall mean (± 1 *s*) of 1.076 ± 0.011. The mean values ($n = 9$) for individual periods of collection from 1989 to 1998 are plotted in Fig. 2, displaying an average increase of 0.2% (~ 0.002) in $^{206}Pb/^{207}Pb$ per year over the decade. The mean of 1.065 ± 0.0026 for the October/November 1994 samples is very close to the 1.067 ± 0.007 reported for leaded petrol purchased in Southampton, south England, in November/December 1994.[14]

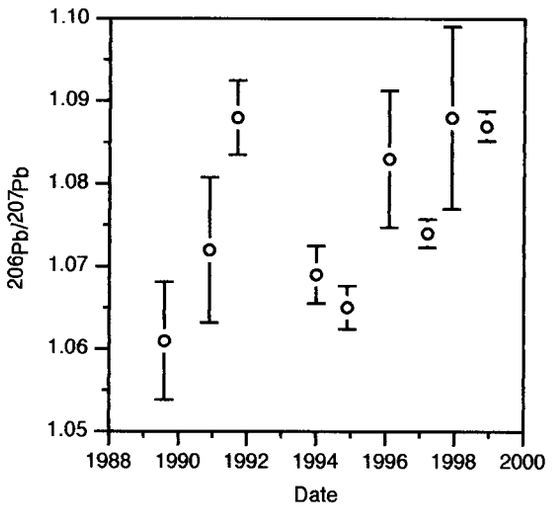

Fig. 2 Mean (± 1 *s*) $^{206}Pb/^{207}Pb$ ratios of leaded petrol for various collection periods in Edinburgh from 1989 to 1998 (see Table 1 for details).

Rainwater

Of the 47 rainwater samples collected across Scotland in December 1997 and January 1998, 74% had a lead concentration below 5 μg l^{-1}, with median and maximum concentrations of 2.9 and 29.3 μg l^{-1}, respectively. Of the 68 rainwater samples collected by open gauge at Glensaugh, Hartwood and Sourhope from November 1997 to December 1998, 97% had a lead concentration below 5 μg l^{-1}, with median and maximum concentrations of 1.0 and 8.8 μg l^{-1}, respectively. Corresponding data for the 30 filter gauge samples were 60% < 5 μg l^{-1}, with median and maximum concentrations of 4.1 and 14.9 μg l^{-1}, respectively.

Scotland. The individual $^{206}Pb/^{207}Pb$ results for rainwater collected across Scotland in December 1997 ($n = 22$) and January 1998 ($n = 25$) are listed in Table 2. The ratios ranged from 1.112 ± 0.0028 at Buchlyvie in January 1998 to 1.218 ± 0.0072 at Stirling in January 1998. Almost 79% of

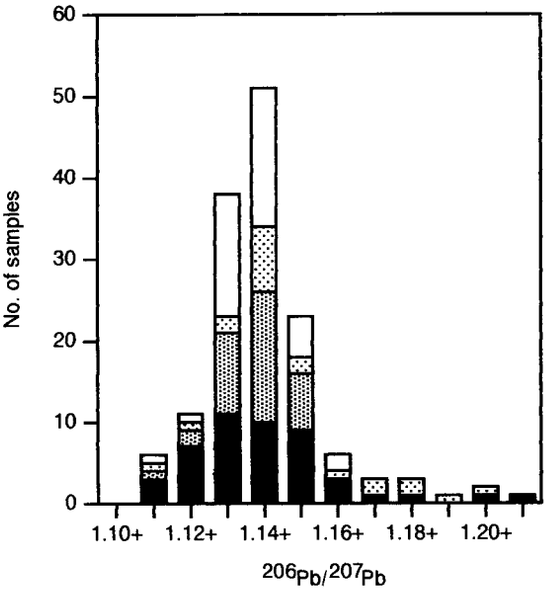

Fig. 3 Histogram of $^{206}Pb/^{207}Pb$ ratios for rainwater samples collected at the 25 sampling sites in Scotland during December 1997 and January 1998 (■) and at the three long-term rainwater collection sites, Glensaugh (□), Hartwood (▨) and Sourhope (▩), from November 1997 to December 1998.

the results, however, were between 1.120 and 1.159 (Fig. 3), with an overall mean (± 1 *s*) of 1.144 ± 0.021. The averages for December 1997 and January 1998 of 1.145 ± 0.014 and 1.144 ± 0.026, respectively, were indistinguishable. There was, however, an apparent geographical trend, with the ratios (Fig. 1) from the southwest (21–25) averaging 1.132 ± 0.010 ($n = 10$; $9 < 1.144$, $1 > 1.144$), from the central belt (7, 11–18) 1.137 ± 0.024 ($n = 16$; $13 < 1.144$, $3 > 1.144$), from the north/northwest (1, 2, 4–6) 1.150 ± 0.008 ($n = 10$; $1 < 1.144$, $9 > 1.144$), and from the east (3, 8–10, 19, 20) 1.162 ± 0.020 ($n = 11$; $0 < 1.144$, $11 > 1.144$). It should be noted, however, that these geographical boundaries, for example between the central belt and the east, are somewhat arbitrary.

Glensaugh, Hartwood and Sourhope. The individual $^{206}Pb/^{207}Pb$ results for rainwater collected at the long-term sites of Glensaugh (northeast Scotland), Hartwood (central belt) and Sourhope (southeast Scotland) from November 1997 to December 1998 are listed in Table 3. On 22 occasions, pairs of samples from both open and filter gauges were available. Whereas 11 of the 14 respective results originating from Glensaugh or Sourhope agreed to within ± 1 *s*, none of the eight respective results from Hartwood were within ± 1 *s* of each other. The concentrations of lead were greater in the filter gauge samples for 20 of the 22 pairs, typically (16/20) by a factor of 1 to 5. Overall, the average $^{206}Pb/^{207}Pb$ ratios (± 1 *s*) for the different sites and modes of collection were similar, with 1.140 ± 0.010 ($n = 27$) and 1.144 ± 0.008 ($n = 14$) for open gauge and filter gauge, respectively, at Glensaugh, 1.141 ± 0.010 ($n = 8$) for filter gauge at Hartwood, and 1.140 ± 0.008 ($n = 28$) and 1.147 ± 0.008 ($n = 8$), respectively, at Sourhope. The sole exception was the value of 1.164 ± 0.024 ($n = 13$) for open gauge at Hartwood. The latter samples, in contrast to the others, displayed some seasonal variations, the $^{206}Pb/^{207}Pb$ ratios being greatest in winter (December/January/February) and spring (March/April/May), with mean values (± 1 *s*) of 1.172 ± 0.012 ($n = 4$) and 1.192 ± 0.015 ($n = 3$), respectively, and lowest in summer (June/July/August) and autumn (September/October/November), with mean values (± 1 *s*) of 1.141 ± 0.016 ($n = 3$) and 1.148 ± 0.017 ($n = 3$), respectively. Although there was a statistically significant ($p < 0.01$, *t*-test) difference between the mean values of 1.180 ± 0.016 for December–May and 1.145 ± 0.015 for June–November, there is no obvious reason why only the open gauge, and not the filter gauge, samples at Hartwood vary seasonally in $^{206}Pb/^{207}Pb$.

For Glensaugh, 90% of all samples collected had $^{206}Pb/^{207}Pb$ ratios in the range 1.130–1.159, with corresponding figures of 57% for Hartwood and 92% for Sourhope. For the total of 98 samples collected at the three long-term sites, almost 88% of the $^{206}Pb/^{207}Pb$ ratios were between 1.120 and 1.159, compared with 79% for the Scotland December 1997/January 1998 samples (Fig. 3). Taken together, the complete set of rainwater samples ($n = 145$) collected at all sites in Scotland from November 1997 to December 1998 had a mean $^{206}Pb/^{207}Pb$ ratio (± 1 *s*) of 1.144 ± 0.017, with 85% of values lying between 1.120 and 1.159.

Pine needles and atmospheric particulates

For Scotland, pine needles of 1985 growth from rural locations in the north displayed a mean $^{206}Pb/^{207}Pb$ ratio (± 1 *s*) of 1.113 ± 0.005 ($n = 4$), indistinguishable from the 1.118 ± 0.006 ($n = 10$) recorded for atmospheric particulates collected at the predominantly northern rural locations in 1985 (Table 4). In contrast, urban atmospheric particulates collected in Glasgow in 1985 had a lower mean $^{206}Pb/^{207}Pb$ ratio (± 1 *s*) of 1.085 ± 0.012 ($n = 4$), a value similar to the 1.099 ± 0.007 ($n = 7$) found for the same city in 1991–1992 and the 1.092 ± 0.011 ($n = 14$) reported for urban Edinburgh in 1990–1991[42] (Table 4), when the mean $^{206}Pb/^{207}Pb$ ratio of leaded petrol sold in the city was 1.079 ± 0.011 ($n = 7$) (Table 1).

Elsewhere in Britain, the mean $^{206}Pb/^{207}Pb$ ratio (± 1 *s*) of atmospheric particulates from rural Gisburn in northwest England in 1985 was 1.108 ± 0.018 ($n = 5$), similar to the corresponding Scottish average and to the values for two 1985 pine needle samples from southeast England (Table 4).

On mainland Europe, the mean $^{206}Pb/^{207}Pb$ ratio (± 1 *s*) for pine needles from four sites in the Netherlands and Germany from 1982 to 1986 was 1.126 ± 0.006 ($n = 8$), slightly higher than the overall mean (± 1 *s*) of 1.112 ± 0.010 ($n = 21$) for the British pine needle and rural atmospheric particulate values for the period 1985–1986 (Table 4). The average $^{206}Pb/^{207}Pb$ ratio (± 1 *s*) of 1.097 ± 0.005 for atmospheric particulates in the Channel Islands in 1989 was closer to the values observed for atmospheric particulates ($n = 25$) in urban Glasgow and Edinburgh from 1985 to 1992, when 52% lay between 1.090 and 1.099 and 76% between 1.080 and 1.099 (Table 4).

Discussion

For the samples of this study collected in Scotland, Fig. 4 displays the mean $^{206}Pb/^{207}Pb$ ratios (± 1 *s*) for petrol (1989–1998, P), urban atmospheric particulates in 1985 (APU1) and in 1990–1992 (APU2), rural atmospheric particulates in 1985 (APR) and rainwater in 1997–1998 (RW2). Also included are the mean $^{206}Pb/^{207}Pb$ ratios (± 1 *s*) for rainwater (1.120 ± 0.016) collected at the three long-term sites in Scotland in 1989–1991 (RW1)[35] and for coal (1.181 ± 0.011) collected at 30 sites in Scotland.[43] The strong influence of car exhaust emissions of lead, originating from the comparatively ^{206}Pb-depleted Australian lead ($^{206}Pb/^{207}Pb \sim 1.04$) used with British Columbian lead ($^{206}Pb/^{207}Pb \sim 1.16$) as the main source[3] of alkyllead manufacture for leaded petrol ($^{206}Pb/^{207}Pb = 1.076 \pm 0.011$), upon atmospheric lead in the urban environment is readily seen from the $^{206}Pb/^{207}Pb$ ratios for APU1 and APU2 of 1.085 ± 0.012 and 1.094 ± 0.010, respectively. That rural environments remote from urban centres are less strongly influenced by such emissions is reflected in the $^{206}Pb/^{207}Pb$ ratio of 1.118 ± 0.006 for APR compared with 1.085 ± 0.012 for APU1, both for 1985, and by the $^{206}Pb/^{207}Pb$ ratio of 1.120 ± 0.016 for RW1 (Glensaugh, Hartwood and Sourhope) in 1989–1991[35] compared with 1.094 ± 0.010 for APU2 in 1990–1992. Similarly, with respect to RW2, the mean $^{206}Pb/^{207}Pb$ ratio of 1.150 ± 0.008 for rainwater

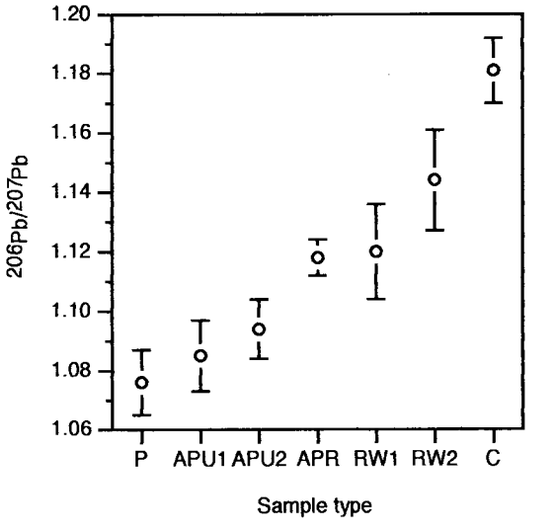

Fig. 4 Mean (± 1 *s*) $^{206}Pb/^{207}Pb$ ratios for petrol (1989–1998, P), urban atmospheric particulates (1985, APU1; 1990–1992, APU2), rural atmospheric particulates (1985, APR), rainwater (1989–1991, RW1; 1997–1998, RW2) and coal (C) from Scotland.

Table 5 Comparison of $^{206}Pb/^{207}Pb$ ratios in rainwater from Scotland, 1989–1991 to 1997–1998

Location	Date of collection	n	$^{206}Pb/^{207}Pb$ (± 1 s)	
			Range	Mean
Glensaugh	1989–1991[35]	11	1.101–1.152	1.119 ± 0.013
	1997–1998 (O)	27	1.113–1.163	1.140 ± 0.010
	1997–1998 (F)	14	1.135–1.161	1.144 ± 0.008
Hartwood	1989–1991[35]	11	1.104–1.153	1.129 ± 0.014
	1997–1998 (O)	13	1.123–1.207	1.164 ± 0.024
	1997–1998 (F)	8	1.118–1.149	1.141 ± 0.010
Sourhope	1989–1991[35]	9	1.081–1.132	1.110 ± 0.018
	1997–1998 (O)	28	1.112–1.153	1.140 ± 0.008
	1997–1998 (F)	8	1.129–1.155	1.147 ± 0.008
Scotland (Table 2)	Dec. 1997–Jan. 1998	47	1.112–1.218	1.144 ± 0.021
Scotland (all)	1997–1998	145	1.112–1.218	1.144 ± 0.017

in December 1997/January 1998 from the most remote and rural of the Scottish locations, the north/northwest, was greater than that from the densely populated central belt, *viz.* 1.131 ± 0.010, excluding the outlier from Stirling for January 1998 (Table 2).

An increase in the atmospheric $^{206}Pb/^{207}Pb$ ratio in Scotland from 1989–1991 to 1997–1998 of $\sim$0.02–0.03 is indicated by the summary data for Glensaugh, Hartwood and Sourhope and for Scotland overall in Table 5. Using the averages (± 1 s) of 1.120 ± 0.016 ($n = 31$) and 1.144 ± 0.017 ($n = 145$) based on all individual 1989–1991 and 1997–1998 data, respectively, the statistically significant ($p < 0.01$, t-test) increase in the atmospheric $^{206}Pb/^{207}Pb$ ratio is 0.024 ± 0.023. Over the same time period, the $^{206}Pb/^{207}Pb$ ratio for petrol increased ($p < 0.05$, t-test) by 0.013 ± 0.015 from 1.075 ± 0.013 (1989–1991) to 1.088 ± 0.007 (late 1997–1998). This suggests that the reduction in the emission of lead to the atmosphere from car exhausts from 2.6×10^3 tonnes in 1989 to 0.8×10^3 tonnes in 1997, when the consumption of unleaded petrol accounted for 71.9% of sales,[39] has contributed to the observed increase in the $^{206}Pb/^{207}Pb$ ratio for rainwater in Scotland.

Source apportionment calculations using an equation[6,44] such as

$$R_A = R_P X_{PA} + R_O X_{OA} \quad (1)$$

where R_A, R_P and R_O are the $^{206}Pb/^{207}Pb$ ratios for the atmosphere, leaded petrol and other sources, respectively, and X_{PA} and X_{OA} ($= 1 - X_{PA}$) are the fractional contributions of leaded petrol and other sources of lead, respectively, to atmospheric lead, can be used to estimate the influence of car exhaust emissions of lead upon the atmospheric lead burden. This assumes that leaded petrol is the predominant source of lead emissions with the characteristic isotopic signature influenced by ^{206}Pb-depleted Australian lead and also relies upon estimates of the $^{206}Pb/^{207}Pb$ ratios for other sources. For the latter, values of 1.17 (corresponding, historically, to the $^{206}Pb/^{207}Pb$ ratio of the principal indigenous lead ore deposits in Scotland and the UK,[1] and to the $^{206}Pb/^{207}Pb$ ratio of anthropogenic lead deposited from the atmosphere during the 19th century, as measured in ombrotrophic peat bogs and freshwater lake sediments[16,17]), 1.18 (corresponding to the typical $^{206}Pb/^{207}Pb$ ratio of coal,[43] once a major source of lead to the atmosphere, but now in decline and a minor component) and 1.19 (corresponding, approximately, to the average "geochemical" signature of lead in the Earth's crust, and thus broadly representative of uncontaminated soils[21,45]) are initially taken here. Thus, using 1.088 for R_P, 1.144 for R_A, and R_O values of 1.17, 1.18 and 1.19, values of X_{PA} are calculated to be 0.32, 0.39 and 0.45, respectively, for 1997–1998. This contrasts with corresponding values for X_{PA} of 0.53, 0.57 and 0.61 when the 1989–1991 values of 1.075 for R_P and 1.120 for R_A are used. When the APU2 $^{206}Pb/^{207}Pb$ ratio of 1.094 is used for R_A in 1990–1992, along with the mean $^{206}Pb/^{207}Pb$ ratio of 1.079 for petrol in 1990–1991 as R_P, the corresponding values are 0.84, 0.85 and 0.86. If the mean rainwater $^{206}Pb/^{207}Pb$ ratio for the central belt (excluding the Stirling outlier) of 1.131 is used for R_A, along with 1.088 for R_P in December 1997/January 1998, the calculated values for X_{PA} are 0.48, 0.53 and 0.58. Thus, on this basis, the contribution of car exhaust emissions of lead from leaded petrol to atmospheric lead in Scotland from the late 1980s/early 1990s until 1998 has declined from 53–61% to 32–45% (using rainwater data from the long-term sites and across Scotland), and, with respect to the urban environment, from 84–86% (using urban atmospheric particulate data) to perhaps 48–58% (using rainwater data from the central belt). AEA Technology[46] estimates that the contribution of lead from petrol to UK emissions of lead to the atmosphere was 86% (2185 of 2703 tonnes) in 1990, 79% in 1991, 77% in 1992, 75% in 1993 and 74% (1295 of 1755 tonnes) in 1994. On the basis of lead isotope measurements on urban particulate matter, Monna *et al.*[14] estimated that 61–84% of lead at a city centre site and 56–74% of lead at a suburban site in Southampton, south England, in 1994 were derived from petrol combustion. The estimated emission of lead from car exhausts to the atmosphere fell further to 0.8×10^3 tonnes in 1997.[39]

With respect to estimation of the contribution of lead from petrol to the emissions of lead to the atmosphere, the above approach based on the isotopic characterization of petrol lead and atmospheric lead does not take into account the likelihood that the possible uniqueness of the source lead isotopic signature, defined in terms of the geochemical origins of the lead in the parent material, will not be restricted to one particular anthropogenic source in terms of the mode or pathway of release to the atmosphere. For example, the smelting of lead ores used to produce lead for the manufacture of alkyllead additives will release lead to the atmosphere of the same isotopic signature as car exhaust emissions of lead from leaded petrol. For 1994, AEA Technology[46] estimated that emissions of lead to the atmosphere in the UK comprised 1295 tonnes from petrol lead, 149 tonnes from waste-related sources, including incineration of sewage, tyres and clinical wastes, 140 tonnes from non-ferrous metal (including lead) production, 102 tonnes from coal (91%) and oil (9%) burning, 46 tonnes from iron and steel production, and 22 tonnes from industrial processes such as cement, glass and coke production. Some of these sources (*e.g.* waste incineration, recycling and refining of battery lead), which will increase in relative importance[47] as emissions of lead from car exhausts continue to fall with increasing consumption of unleaded petrol and the banning of leaded petrol in the UK in 2000, may be of ill-defined or varying lead isotopic signature. Monna *et al.*,[14] however, found a mean $^{206}Pb/^{207}Pb$ ratio of 1.149 ± 0.005 (range 1.143–1.155) for French urban incinerator ashes in 1993–1994, similar to the

1.142–1.159 found in Germany by Hamester *et al.*[12] The effect of using this value as the predominant "industrial" signature (*i.e.* as R_O) in source apportionment eqn. (1) would be to reduce the calculated contribution of car exhaust emissions of lead to atmospheric lead even further, and there is recent evidence from a New York study[48] that municipal waste incineration releases of lead have been seriously underestimated in the past.

The approach adopted in this study does not take into account likely differences, depending upon proximity to major sources, in the atmospheric inventory of lead at different locations. It also neglects the possibility that clouds, as with the movement of aerosol-entraining air masses, can transport lead from much further afield, with the result that wet precipitation may not be just washing out lead released to the atmosphere in the geographical area where the rainwater samples are collected. Whether or not the slightly elevated mean $^{206}Pb/^{207}Pb$ ratio of 1.162 ± 0.020 for rainwater in eastern Scotland in December 1997/January 1998, supported to some extent by the average Glensaugh/Sourhope $^{206}Pb/^{207}Pb$ ratio of 1.149 ± 0.008 for that period, could reflect the influence of air masses from the continent of Europe to the east is difficult to assess, but typical $^{206}Pb/^{207}Pb$ ratios of 1.148–1.162 and 1.160–1.185 have been reported for air masses from the regions of USSR/Finland and Eastern Europe,[4] respectively, and $^{206}Pb/^{207}Pb$ ratios ranging from 1.109 up to 1.204 were observed in aerosols above Helgoland in the southeastern North Sea during a 2 week period in April 1988.[45] More recently in Western Europe, however, it is worth noting that there was a shift in the mean $^{206}Pb/^{207}Pb$ ratio of aerosols collected from a rural area in the Nord-Pas de Calais region along the English Channel from 1.108 ± 0.005 in 1982–1983 to 1.148 ± 0.003 in 1994, paralleled by similar variations from 1.115 ± 0.008 in 1981–1989 to 1.143 ± 0.006 in 1992–1995 in urban aerosols in France and from 1.094 in 1985 to 1.135 ± 0.002 in 1995 along French highways.[33] These increases from values similar to those found in our study for pine needles in Western European countries and for atmospheric particulates in the Channel Islands during the 1980s (Table 4) are analogous to those observed here for Scotland since the 1980s and can also be attributed to the declining influence of lead emissions as a consequence of the phasing out of leaded petrol in France.

Conclusions

The $^{206}Pb/^{207}Pb$ ratio of rainwater in Scotland has increased during the 1990s from 1.120 ± 0.016 in 1989–1991 to 1.144 ± 0.017 in 1997–1998, attributable partially to an increase in the $^{206}Pb/^{207}Pb$ ratio of leaded petrol, but mainly to a reduction in the car exhaust emissions of lead to the atmosphere resulting from the increased consumption of unleaded petrol and the phasing out of alkyllead additives. In view of the wide ranging use made of anthropogenic lead isotopic ratios as tracers and source indicators in environmental and earth sciences, it will be important to continue monitoring atmospheric $^{206}Pb/^{207}Pb$ ratios at this time of change and to identify contributions of lead from sources, such as incinerators, which may increase in relative importance.

Acknowledgements

We thank J. N. Cape, NERC ITE, and D. Smith, NRPB, for provision of certain samples, C. L. Sugden, K. Cotton, J. L. Hitchen, A. A. Pott, C. F. Catto, M. Emery and N. Kulasuriya for assistance with collection and preparation of most samples, and A. B. MacKenzie, M. McCartney, T. M. Shimmield and K. Sampson for those ICP-MS analyses carried out using the VG PQ 1 and 2 at SURRC, East Kilbride.

References

1 S. Moorbath, *Philos. Trans. R. Soc. London, Ser. A*, 1962, **254**, 295.
2 T. J. Chow, in *Isotope Ratios as Pollutant Source and Behaviour Indicators*, IAEA, Vienna, 1975, pp. 95–107.
3 H. T. Delves, *Chem. Brit.*, 1988, **24**, 1009.
4 J. F. Hopper, H. B. Ross, W. T. Sturges and L. A. Barrie, *Tellus*, 1991, **43B**, 45.
5 M. Keinonen, *Sci. Total Environ.*, 1992, **113**, 251.
6 J. G. Farmer, C. L. Sugden, A. B. MacKenzie, G. H. Moody and M. Fulton, *Environ. Technol.*, 1994, **15**, 593.
7 W. T. Sturges and L. A. Barrie, *Atmos. Environ.*, 1989, **23**, 1645.
8 W. T. Sturges and L. A. Barrie, *Atmos. Environ.*, 1989, **23**, 2513.
9 H. Mukai, N. Furuta, T. Fujii, Y. Ambe, K. Sakamoto and Y. Hashimoto, *Environ. Sci. Technol.*, 1993, **27**, 1347.
10 W. T. Sturges, J. F. Hopper, L. A. Barrie and R. C. Schnell, *Atmos. Environ.*, 1993, **27A**, 2865.
11 F. E. Grousset, C. R. Quetel, B. Thomas, P. Buat-Menard, O. F. X. Donard and A. Bucher, *Environ. Sci. Technol.*, 1994, **28**, 1605.
12 M. Hamester, H. Stechmann, M. Steiger and W. Dannecker, *Sci. Total Environ.*, 1994, **146/147**, 321.
13 M. Chiaradia, B. L. Gulson, M. James, C. W. Jameson and D. Johnston, *Atmos. Environ.*, 1997, **31**, 3511.
14 F. Monna, J. Lancelot, I. W. Croudace, A. B. Cundy and J. T. Lewis, *Environ. Sci. Technol.*, 1997, **31**, 2277.
15 J. R. Graney, A. N. Halliday, G. J. Keeler, J. O. Nriagu, J. A. Robbins and S. A. Norton, *Geochim. Cosmochim. Acta*, 1995, **59**, 1715.
16 J. G. Farmer, L. J. Eades, A. B. MacKenzie, A. Kirika and A. E. Bailey-Watts, *Environ. Sci. Technol.*, 1996, **30**, 3080.
17 J. G. Farmer, A. B. MacKenzie, C. L. Sugden, P. J. Edgar and L. J. Eades, *Water, Air, Soil Pollut.*, 1997, **100**, 253.
18 W. Shotyk, D. Weiss, P. G. Appleby, A. K. Cheburkin, R. Frei, M. Gloor, J. D. Kramers, S. Reese and W. O. van der Knaap, *Science*, 1998, **281**, 1635.
19 C. E. Dunlap, E. Steinnes and A. R. Flegal, *Earth Planet. Sci. Lett.*, 1999, **167**, 81.
20 D. Weiss, W. Shotyk, P. G. Appleby, J. D. Kramers and A. K. Cheburkin, *Environ. Sci. Technol.*, 1999, **33**, 1340.
21 J. R. Bacon, M. L. Berrow and C. A. Shand, *Int. J. Environ. Anal. Chem.*, 1992, **46**, 71.
22 J. R. Bacon, M. L. Berrow and C. A. Shand, *Int. J. Environ. Anal. Chem.*, 1995, **59**, 253.
23 N. Walraven, B. J. H. van Os, G. Th. Claver, J. H. Baker and S. P. Vriend, *J. Geochem. Explor.*, 1997, **59**, 47.
24 J. R. Bacon, K. C. Jones, S. P. McGrath and A. E. Johnston, *Environ. Sci. Technol.*, 1996, **30**, 2511.
25 S. A. Watmough, R. J. Hughes and T. C. Hutchinson, *Environ. Sci. Technol.*, 1999, **33**, 670.
26 G. Aberg, J. M. Pacyna, H. Stray and B. L. Skjelkvale, *Atmos. Environ.*, 1999, **33**, 3335.
27 K. J. Rosman, C. Ly and E. Steinnes, *Environ. Sci. Technol.*, 1998, **32**, 2542.
28 D. Weiss, W. Shotyk, J. D. Kramers and M. Gloor, *Atmos. Environ.*, 1999, **33**, 3751.
29 K. J. R. Rosman, W. Chisholm, C. F. Boutron, J.-P. Candelone and U. Gorlach, *Nature*, 1993, **362**, 333.
30 K. J. R. Rosman, W. Chisholm, S. Hong, J.-P. Candelone and C. F. Boutron, *Environ. Sci. Technol.*, 1997, **31**, 3413.
31 H. Maring, D. M. Settle, P. Buat-Menard, F. Dulac and C. C. Patterson, *Nature*, 1997, **300**, 154.
32 A. Veron and T. M. Church, *J. Geophys. Res.*, 1997, **102**, 28 049.
33 A. Veron, P. Flament, M. L. Bertho, L. Alleman, R. Flegal and B. Hamelin, *Atmos. Environ.*, 1999, **33**, 3377.
34 G. T. Shen and E. A. Boyle, *J. Geophys. Res.*, 1988, **93**, 15715.
35 J. R. Bacon and D. C. Bain, *Environ. Geochem. Health*, 1995, **17**, 39.
36 Y. Erel, A. Veron and L. Halicz, *Geochim. Cosmochim. Acta*, 1997, **61**, 4495.
37 Y. Gelinas and J.-P. Schmit, *Environ. Sci. Technol.*, 1997, **31**, 1968.
38 A. B. MacKenzie, J. G. Farmer and C. L. Sugden, *Sci. Total Environ.*, 1997, **203**, 115.
39 DETR, *Digest of Environmental Statistics No. 20*, The Stationery Office, London, 1998.
40 A. Cocherie, P. Negrel, S. Roy and C. Guerrot, *J. Anal. At. Spectrom.*, 1998, **13**, 1069.
41 W. J. Price, *Spectrochemical Analysis by Atomic Absorption*, Heyden and Son Ltd., London, 1979, p. 240.

42 C. L. Sugden, J. G. Farmer and A. B. MacKenzie, *Environ. Geochem. Health*, 1993, **15**, 59.
43 J. G. Farmer, L. J. Eades and M. C. Graham, *Environ. Geochem. Health*, 1999, **21**, 257.
44 H. T. Delves and M. J. Campbell, *Environ. Geochem. Health*, 1993, **15**, 75.
45 M. Kersten, U. Forstner, P. Krause, M. Kriews, W. Dannecker, C.-D. Garbe-Schonberg, M. Hock, U. Terzenbach and H. Graßl, in *Impact of Heavy Metals in the Environment*, ed. J.-P. Vernet, Elsevier, Amsterdam, 1992, vol. 2, pp. 311–325.
46 AEA Technology, *http://www.aeat.co.uk/netcen/airqual/emissions/index/html*, 1998.
47 J. O. Nriagu, *Science*, 1998, **281**, 1622.
48 S. N. Chillrud, R. F. Bopp, J. H. Simpson, J. M. Ross, E. L. Shuster, D. A. Chaky, D. C. Walsh, C. C. Choy, L.-R. Tolley and A. Yarme, *Environ. Sci. Technol.*, 1999, **33**, 657.

Paper a907558e